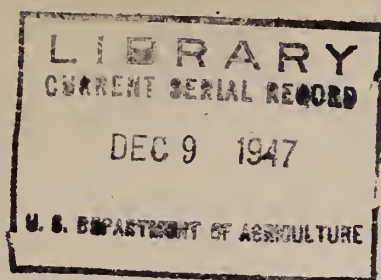


Historic, archived document

Do not assume content reflects current scientific knowledge, policies, or practices.

4

LIBRARY
JUN 30 1948
68 CENTRAL ST. & 12TH ST.



Stress Relaxation of Cotton and Rayon Cords at Constant Length*

Edward G. Burleigh and Helmut Wakeham**

Southern Regional Research Laboratory,† New Orleans, Louisiana

RECENT advances in the science of high polymers have resulted in the development of theories which permit interpretation of textile properties in terms of molecular quantities. These theories make possible evaluation of some of the molecular constants required to correlate satisfactorily the physical and chemical behavior of a textile fiber with the properties of the molecules of which it is composed. The present paper demonstrates the application of stress-relaxation data to the Tobolsky-Eyring [26] theory of mechanical properties of high-polymeric materials for the purpose of determining certain molecular constants characteristic of cellulose fibers.

The investigation of stress relaxation at constant deformation of textile materials has been seriously neglected despite the advantages of such a study in adding to our knowledge of textile behavior. Experimental data which have been reported for glass filaments [9], rubber [2, 15, 21, 25, 27], gelatin gels [4], lead [28], steel [29], and polyvinyl acetate [17] have only limited application to the problem of textiles. Smith and Eisenschitz [24] investigated stress relaxations of viscose rayon, cellulose acetate, and silk. They attempted to interpret their results

in terms of the Boltzmann "after-effect theory," which they found permits only an "approximation to the actual behavior of rayon." On the other hand, the reviews by Press [23], Leaderman [10], and Lyons [11] indicate a wealth of flow and creep-recovery data which, because of the complexity of the phenomena involved, cannot be used in evaluating molecular constants as readily as stress-relaxation data. As Lyons points out, stress relaxation eliminates strain as a variable and permits investigation of "the adjustments taking place at the micellar and molecular levels, without the complication of concomitant deformation in the fiber substance."

The present report is of just such an investigation. In it a new method for evaluating stress relaxation is described, and the results obtained are interpreted in terms of current molecular concepts of the structure of cellulose fibers.

Theory

Three types of motion in a fiber are postulated in the reaction-rate theory of elasto-viscous behavior as outlined by Tobolsky and Eyring [25, 26]: motion due to decay of the primary structural elements of the fiber network; motion due to relaxation of secondary cross bonds permitting units of the network structure to slip on the application of stress; and motion of the mobile segments of the long molecules or groups of molecules. Equations based on a modi-

* Read before the Fiber Society, New Orleans, February 20, 1947.

** Dr. Wakeham's present address: Institute of Textile Technology, Charlottesville, Virginia.

† One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

fication of the Maxwell-Wiechert theory have been written for each of these types of motion. Finally, the theory has been extended and applied to textile fibers as outlined by Eyring and coworkers [6] at the Textile Foundation Laboratories.

In the experimental determination of stress relaxation, the substance is rapidly stretched to a given length which is held fixed while the stress decay with time is measured. In this type of experiment it is believed that the stress due to motion of the mobile segments decays very rapidly so that it is not observable. The stress due to the primary structural elements of the network units, on the other hand, decays very slowly, if at all. The observed stress decay is, then, due to the relaxation of secondary network bonds; and a study of stress relaxation under these conditions should yield information concerning the nature of such bonds.

The equation of motion for secondary bond relaxation is, in the notation of Tobolsky and Eyring [26],

$$\frac{ds}{dt} = \frac{1}{G} \frac{df}{dt} + A \sinh Bf, \quad (1)$$

where (ds/dt) is the rate of change of length with time, (df/dt) is the rate of change of force, f , with time, and G , A , and B are molecular constants defined as:

G = an elastic modulus of the substance,

$$A = 2n\lambda \frac{kT}{h} \exp(-\Delta F^\ddagger/RT), \quad (2)$$

and

$$B = \frac{\lambda}{2NkT}. \quad (3)$$

In this theory it is assumed that there are N parallel flowing units in a square centimeter of fiber cross section, that the distance between successive equilibrium positions of each flowing unit in the direction of stress is λ , that n is the average number of secondary bonds per centimeter which are involved in the movement of each flow unit, and that ΔF^\ddagger is the free energy of activation for movement from one equilibrium position to the next. The other terms in equations (2) and (3) are Boltzmann's constant, $k = 1.371 \times 10^{-16}$ erg/°C; Planck's constant, $h = 6.55 \times 10^{-27}$ erg sec.; the gas constant, $R = 1.987$ cal./mole; and the absolute temperature, T . The force f/N is then the average force on each flowing

unit which tends to favor motion from one equilibrium position to another in the direction of stress.

Since, in the stress-relaxation experiment with constant strain $(ds/dt) = 0$, equation (1) may be integrated to obtain

$$\tanh\left(\frac{Bf}{2}\right) = \tanh\left(\frac{Bf_0}{2}\right) e^{-k't}, \quad (4)$$

where f_0 is the initial stress and $k' = ABG$. Figure 1 is a graph of this hyperbolic tangent decay function where f/f_0 is plotted against the logarithm of $k't$ for different values of $Bf_0/2$.

The constants B and k' in equation (4) may be evaluated from the experimental relaxation curves of f/f_0 plotted against $\log t$. Values of G are obtained from the experimentally determined elastic modulus of the material during a rapid, reversible stress-strain cycle. With these constants it then becomes possible to calculate the number of flow units, N , per square centimeter of fiber cross section and ΔF^\ddagger , providing values may be assigned to the displacement distance, λ , and to the number of bonds, n , per centimeter length of flow unit. These values are obtained from a consideration of cellulose fiber structure and molecular coordination.

Present concepts of the molecular architecture of the cellulose fiber may be summarized as follows [7, 18, 22]: The fiber consists of a structure of long cellulose chains which lie roughly parallel to the long axis of the fiber. In localized regions of the fiber the chains are orientated with respect to each other in such a way as to form a crystalline lattice. The fraction of cellulose which is thus associated in crystalline regions varies from fiber to fiber. For native cotton cellulose this fraction is estimated to be between 60 and 95 percent and for regenerated cellulose between 25 and 85 percent [1, 5, 7, 13, 20]. Because the chain length is but a fraction of the fiber length, stress from one end of the fiber to the other must be transmitted from one chain to its neighbors by means of intermolecular bonds or forces. These forces are probably strongest in the crystalline regions where the chains lie in closest proximity to each other. As stress is applied to the fiber and as slack in the noncrystalline portions is taken up, forces are exerted to cause slippage of the cellulose chains with respect to each other. This slippage is believed to be responsible for stress relaxation under conditions of constant deformation of the fiber.

The dimension of the unit cell of crystalline cellulose in the direction parallel to the cellulose chain is the length of the cellobiose unit, the repeating element in the polymer chain [16]. The cell structure and molecular coordination between chains are such that if one chain moves in the direction of its long axis with respect to its neighbors, it will not reach a position of equal stability until it has moved the length of the cellobiose unit—that is, 10.3 Å. This should, then, be the minimum distance between equilibrium positions of the chain if the crystalline structure is to be preserved.

Hence, we arrive at $\lambda = 10.3 \times 10^{-8}$ cm.

The number of bonds per centimeter, n , may be evaluated from Peirce's investigation [22] of the molecular coordination in both native and regenerated cellulose. He assigns hydroxyl bonds to positions between the chains in the 002 planes of native cellulose and in the 101 planes of the regenerated cellulose. These hydroxyl bonds are the secondary bonds largely responsible for restricting movement of the flow units. In native cellulose there are postulated 4 such bonds per cellobiose unit for those chains in the centers of the unit cells and 6 bonds per cellobiose unit for the chains at the corners of the cells. The average value will then be 5 bonds per cellobiose unit because there are an equal number of units in each position of the cell. Hence, for native cellulose, $n = 5/10.3 \times 10^8$. From similar considerations for the regenerated cellulose, $n = 10/10.3 \times 10^8$.

The probability that the flow unit consists of several chains held together by hydroxyl bonds and van der Waals forces, instead of single chains as assumed in the foregoing evaluations of λ and n , does not seriously affect the application of the Tobolsky-Eyring theory. The distance between equilibrium positions of multiple-chain flow units would still be the length of the cellobiose unit. Although the combination of chains making up the flow unit might result in larger values of n , the minimum values for n would still be those indicated. Since stress slip-

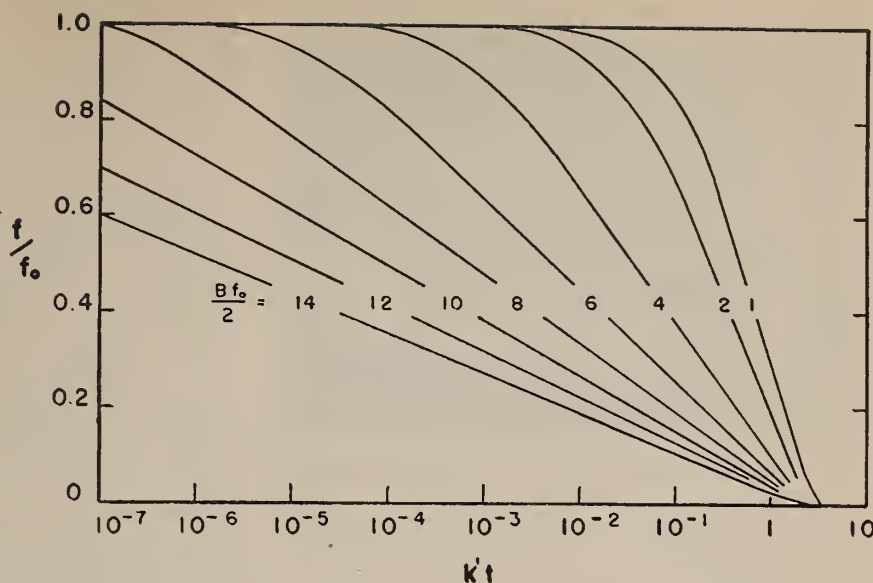


FIG. 1. Hyperbolic tangent decay curves for values of $Bf_n/2$.

page may be expected to occur along lines of least resistance—that is, where the secondary cross links are at a minimum—situations in which n is a minimum will probably predominate. Furthermore, when f_n is large and when the fiber structure is swollen with water so that the interchain hydroxyl bonds are weakened, it seems possible that N may approach the actual number of chains present. Under such conditions the chains may be expected to flow as individual units.

Experimental Data

The bonded metaelectric strain gage is ideally suited for investigations in which the problem is one of either continuous or intermittent measurement of stress [8] over a period of time. Such is the problem in this investigation, in which rapidly decaying stress in a strained cord must be measured as a function of time with the added condition imposed that the length must be held constant. This condition was met by using as the measuring element a strain gage on a metal weighbar attached to the cord; since the elongation in the weighbar was extremely small in comparison with that in the cord, the process of relaxation in the cord can be considered one of essentially constant length.

The gage used with most success in this work was the Baldwin SR-4 strain gage, type A-11, which has a resistance of 120 ohms and a gage factor of 2.10. The gage factor was high enough to give

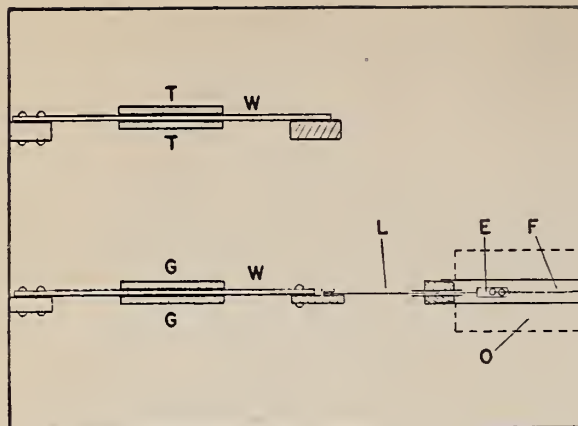


FIG. 2. Schematic diagram of relaxation apparatus. *G*—active gage, *T*—temperature compensator gage, *W*—brass weighbar, *L*—steel-wire leader, *E*—brass tie, *F*—cord, and *O*—oven.

good sensitivity when mounted on a thin weighbar, and the temperature coefficient was sufficiently low to obviate the necessity of precise thermal control beyond that obtainable with an ordinary air-conditioning unit. Room temperature was actually controlled within $\pm 2^\circ\text{F}$.

The gages were mounted longitudinally on weighbars cut from 0.003-inch brass shimstock $4\frac{1}{2}$ inches \times $\frac{3}{8}$ inch, a gage cemented to each side of the strip. Two of these strips, or 4 gages, were assembled to make up a gage network, or measuring unit. One strip was placed horizontally in the apparatus (Figure 2) to carry the tension; hence, the 2 gages bonded to it were "active" gages. Another strip placed directly above and parallel to the first carried no load, and the 2 gages bonded to it acted as temperature compensators. The 4 gages of the measuring unit were wired so as to make up the 4 arms of a Wheatstone bridge (Figure 3), the unbalance of which was a measure of the resistance changes in the active gages brought about when tension was applied to the active strip. The cord to be tested was attached to the free end of the weighbar by means of a steel wire leader, *L* (Figure 2), with stirrup-like brass tie, and the desired tension was applied to the other end of the cord through a similar tie by weights suspended over a ball-bearing pulley. The cord and wire leaders were aligned with the longitudinal axis of the weighbar so that all the load applied to the end of the cord was conveyed to the active gages. The cord itself was inside a long tube

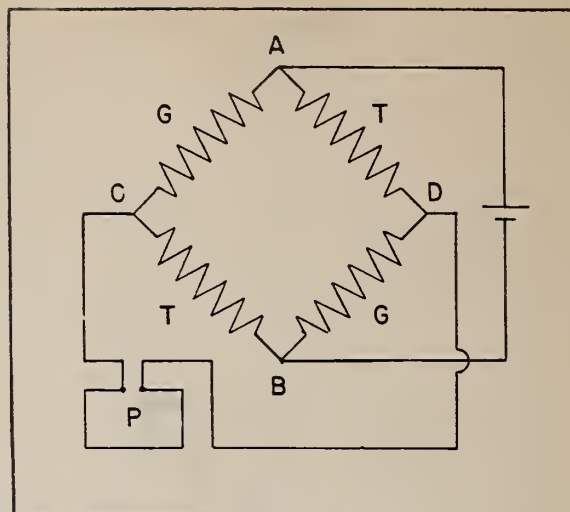


FIG. 3. Diagram of strain-gage circuit. *G*—active gage, *T*—temperature compensator gage, *P*—potentiometer, *A-B*—points across which input e.m.f. is measured, and *C-D*—points across which output e.m.f. is measured.

in an insulated chamber or oven in which the temperature and humidity conditions could be controlled.

The apparatus consisted of a battery of 6 such measuring units so that 6 cords could be tested simultaneously (Figure 4).

A constant electromotive force was applied to the Wheatstone bridge at points *A* and *B* (Figure 3), and the potentiometer measuring circuit measured the output of the gages across points *C* and *D*. Through a double-pole, double-throw switch the potentiometer circuit could also be utilized to measure the applied e.m.f. across points *A* and *B*.

By calibration of the gages under static loads it was confirmed that the e.m.f. output was essentially linear with respect to load [3]. The applied e.m.f. was adjusted through a variable resistance so that the sensitivity of the gage was very nearly 2 pounds per millivolt. The applied e.m.f. required to achieve this sensitivity was in each case approximately 10.5 volts.

It was found that the performance of the gages was materially improved by a "conditioning" for several hours under the load at which the cords were to be tested.

Since the relaxation of stress in a cord is initially a very rapid process, measurements of the gage output during the first few seconds of the relaxation had to be made with considerably greater speed than

is possible with a manually operated potentiometer. Therefore, the early stages of the relaxation were followed by the deflection of the null-indicating galvanometer of the potentiometer circuit, the sensitivity of which was properly adjusted by appropriate series and parallel resistances. By simultaneously photographing with a movie camera the galvanometer and an electric timer having a large sweep second hand, a continuous record was made of the galvanometer deflection throughout the first few seconds of the relaxation. Thus, at any elapsed time the galvanometer deflection could be read from the film record, and from that deflection the drop in e.m.f. output of the gage could be determined. After the first 60 seconds, the relaxation was proceeding slowly enough to be followed by direct readings on the potentiometer.

The cord samples to be tested, 50 centimeters in length, were preconditioned before being inserted in the apparatus. For the dry experiments they were first dried in a vacuum at room temperature for several hours and then placed in the tubes of the test oven under a stream of dry air. Higher moisture contents were attained by conditioning the cords at room humidity. Conditioning to 100 percent relative humidity was achieved by blowing moisture-saturated air through the oven tubes. After suitable conditioning the cords were rapidly stretched at 2 seconds before "zero" time and clamped in position at "zero" time. At the instant of clamping the galvanometer began its rapid deflection corresponding to stress decay in the cord. The record of time and gage e.m.f. was made as described earlier.

Relaxation experiments were made with two tire cords: one a wet-stretched cotton tire cord of 17/4/3 construction, a dry Grex number of 4446, and an oven-dry breaking strength of 2.24 g./Grex; the other a viscose rayon cord of 2200/2 construction, a dry Grex number of 5366, and an oven-dry breaking strength of 2.90 g./Grex. The vacuum-dried cords were relaxed at 25, 110, and 160°C with initial loads of 0.5 g./Grex, and at 25°C with initial loads of 1.0 g. Grex. The moist cords were all relaxed at 25°C with initial loads of 0.5 g./Grex. Several experimental relaxation runs, in some cases as many as nine, were made for each cord at each condition tested. Unfortunately it was not experimentally practical to extend the observations to higher or lower initial loads than 1.0 and 0.5 g./Grex, respectively. At appreciably higher loads too large a

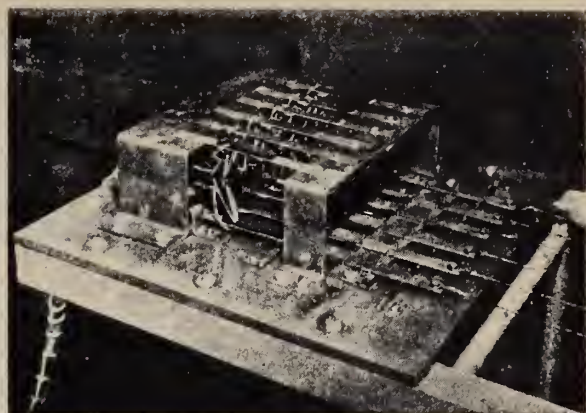


FIG. 4. Photograph of strain-gage units used in stress-relaxation experiments.

percentage of the cords broke upon loading; at lower loads the low sensitivity of the electric gages made the experimental error in stress determination proportionately large.

Results and Discussion

Typical relaxation curves at various conditions are shown in Figure 5 (cotton cord) and Figure 6 (rayon cord).

From the results of such relaxation experiments the constants shown in Table I were calculated. The initial force, f_0 , and the number of cellulose chains, N_c , both per square centimeter of cross section, were evaluated from the Grex number of the cord and the density of crystalline cellulose (1.582 for cotton and 1.595 for rayon) [12, 18]. For a given experiment, the value of $Bf_0/2$ was found by comparing the slope of the experimental curve with the theoretical curves shown in Figure 1; similarly, k' was obtained from the measured displacement necessary to shift the experimental curve to its corresponding theoretical curve. The elastic modulus, G , at each condition for the cord was obtained from the observed modulus of the cord [30] corrected for the intra- and interfiber spaces by multiplying the observed modulus by the ratio of the density of crystalline cellulose to the apparent density of the cord calculated from the cord gage and Grex number. From these data and the values of n and λ described earlier, the constants A , B , N , and ΔF^\ddagger were calculated by means of equations (2), (3), and (4). In addition to these constants, Table I shows values of the ratio N_c/N , which is the average

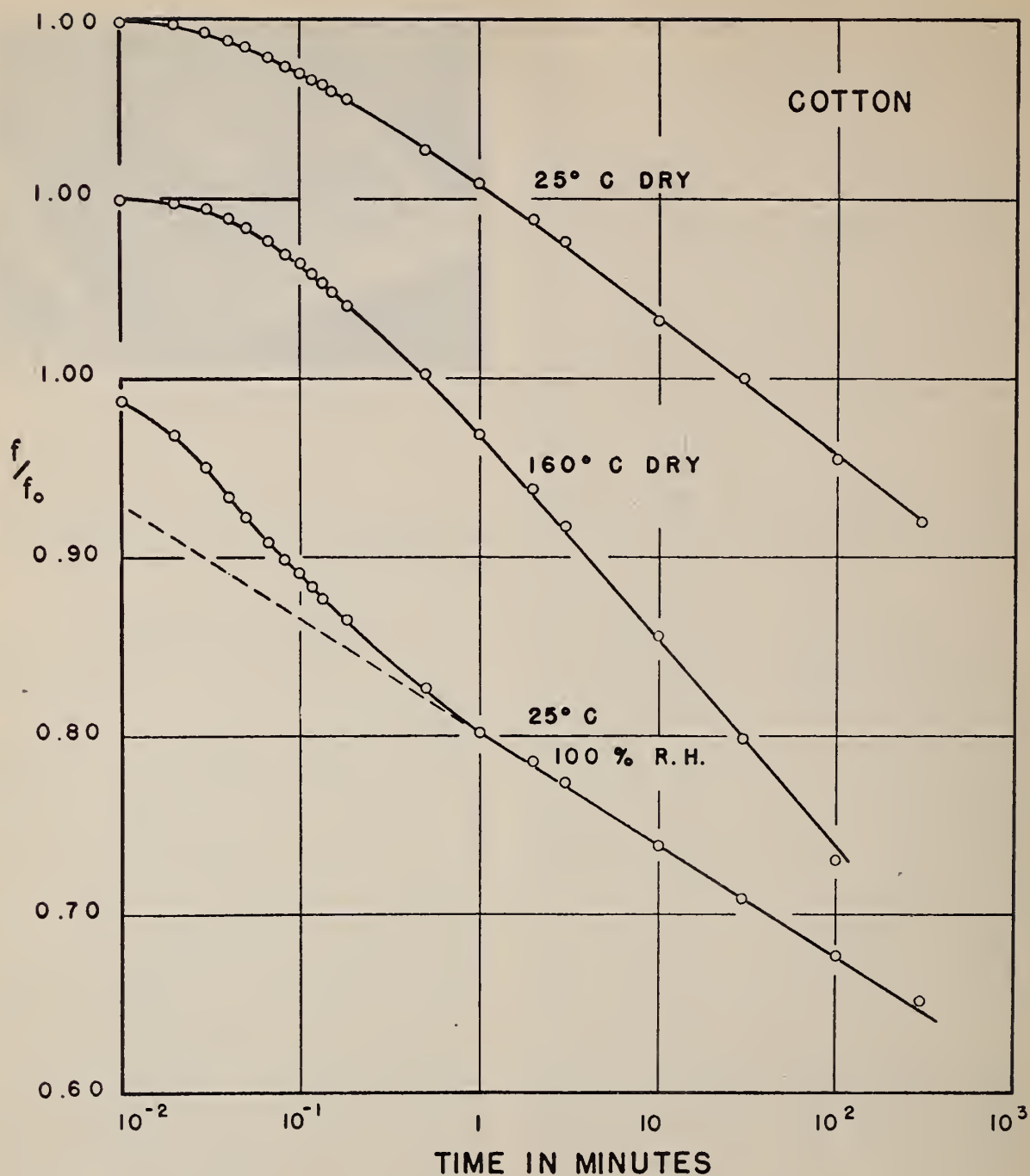


FIG. 5. Experimental stress-relaxation curves for cotton.

number of cellulose chains per flow unit for the cord during the relaxation process.

The authors in making these calculations have assumed that the observed stress relaxation is an

intrafiber process and that the interfiber movement, or slippage, which takes place during the loading to maximum stress, ceases at the instant the cord is clamped at constant length. It seems unlikely that

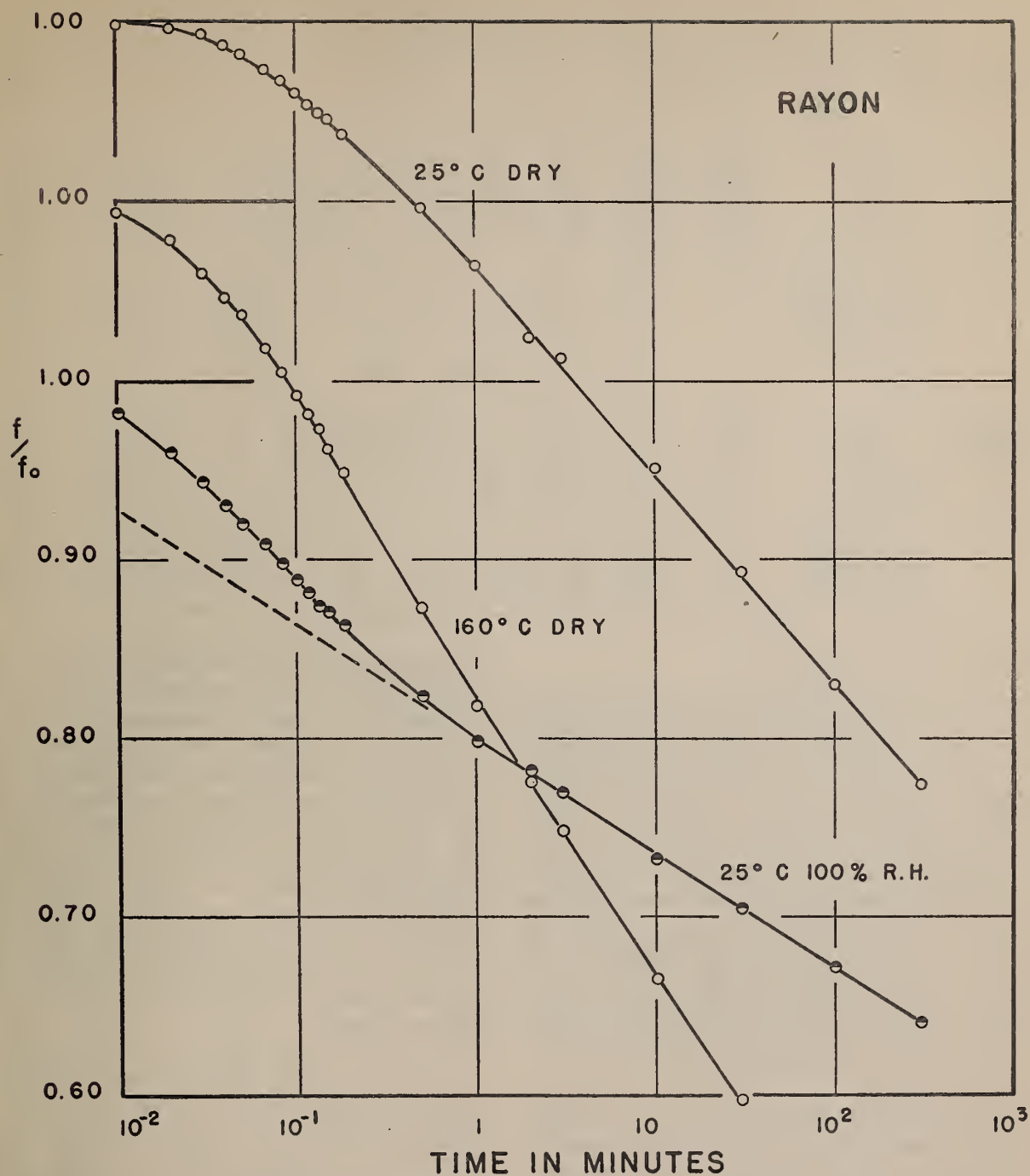


FIG. 6. Experimental stress-relaxation curves for rayon.

interfiber slippage should continue in the same direction after clamping when the stress is decaying. This view is supported by the fact that the rayon cord with continuous filaments showed higher rates

of stress decay than the cotton cord composed of staple fiber showed. If fiber-on-fiber movement were a factor in stress decay, the opposite could logically be expected.

TABLE I. MOLECULAR CONSTANTS FOR STRESS RELAXATION OF COTTON AND RAYON CORDS

Temp. (°C)	Relative humidity	Moisture content (Dry basis)	f_0 (dynes/cm ²) $\times 10^8$	Bf_0 2	B $\times 10^{-8}$	N $\times 10^{13}$	N_c N	k'	G $\times 10^{10}$	A	ΔF^\ddagger (Calories)
For cotton ($N_c = 3.05 \times 10^{14}$)											
25	—	Dry	15.50	16.4	2.11	5.95	5.1	8.0×10^{-15}	7.6	5.0×10^{-18}	42,400
160	—	Dry	7.75	9.2	2.37	3.66	8.3	2.5×10^{-9}	8.7	1.23×10^{-12}	51,250
110	—	Dry	7.75	11.6	2.99	3.27	9.3	4.3×10^{-11}	8.0	1.8×10^{-14}	48,450
25	—	Dry	7.75	13.2	3.41	3.70	8.2	1.24×10^{-12}	7.6	4.8×10^{-16}	39,700
25	37%	4.5%	7.75	12.6	3.25	3.88	7.9	1.11×10^{-11}	8.7	3.9×10^{-15}	38,450
25	70	6.2	7.75	12.4	3.20	3.94	7.7	2.0×10^{-11}	8.3	7.5×10^{-15}	38,100
25	100	25 (approx.)	7.75								
		For f_0'' (max)		17.2	4.44	2.84	10.7	6.9×10^{-15}	5.2	3.0×10^{-18}	42,700
		For f_0' (max)		2.0	0.52	24.40	1.2	6.2	5.2	2.3×10^{-2}	21,050
		For f_0' (min)		1.0	0.26	48.80	0.6	6.7	5.2	5.0×10^{-2}	20,600
For rayon ($N_c = 3.08 \times 10^{14}$)											
25	—	Dry	15.64	12.4	1.58	7.96	3.9	6.0×10^{-11}	8.2	4.6×10^{-14}	37,400
160	—	Dry	7.82	7.2	1.84	4.71	6.5	9.1×10^{-7}	6.1	8.1×10^{-10}	46,300
110	—	Dry	7.82	9.2	2.35	4.17	7.4	6.4×10^{-9}	6.6	4.2×10^{-12}	44,850
25	—	Dry	7.82	10.1	2.58	4.88	6.3	9.1×10^{-10}	7.5	4.7×10^{-13}	36,050
25	37%	8.2	7.82	9.4	2.40	5.26	5.9	6.3×10^{-9}	6.9	3.8×10^{-12}	34,800
25	70	11.9	7.82	9.2	2.35	5.36	5.7	2.1×10^{-8}	6.4	1.4×10^{-11}	34,050
25	100	40 (approx.)	7.82								
		For f_0'' (max)		16.6	4.25	2.97	10.4	2.1×10^{-14}	4.9	9.9×10^{-18}	42,400
		For f_0' (max)		1.7	0.435	29.00	1.1	6.4	4.9	3.0×10^{-2}	21,300
		For f_0' (min)		1.0	0.26	49.20	0.6	6.0	4.9	4.7×10^{-2}	21,050

Effect of Initial Load

The data at 25°C for the dry cords indicate that B is not a constant but decreases as f_0 increases. This effect has also been observed with rubber, for which the function $Bf_0/2$ has been shown experimentally to be a constant independent of initial stress, so that B is inversely proportional to f_0 [25]. The significance of this relationship seems to be that the number of flow units per unit cross section increases with increasing initial stress. Obviously, in the case of cellulose, as N becomes larger it cannot increase beyond the limiting value of $N = N_c$ when the flow units are the individual cellulose chains. If we assume that at high initial loads $Bf_0/2$ has a constant value equal to that observed for the dry cords at 25°C and at initial loads of 1.0 g./Grex, we may calculate f_0^* for the case of $N = N_c$, obtaining for cotton $f_0^* = 7.9 \times 10^9$ dynes/cm² and for rayon $f_0^* = 6.1 \times 10^9$ dynes/cm². These values of f_0^* might be called the force necessary to cause all the cellulose chains to move as individual flow units.

It has been pointed out by several investigators that the theoretical or potential tensile strength of cellulose fibers, based on the force necessary to rupture the primary valence chain in cellulose, is many times the observed tensile strength [14, 19]. Vari-

ous explanations have been advanced to account for this difference. Now it is recognized that the rate of elongation, or flow, in the cellulose fiber is greatly increased as the applied stress is increased. This phenomenon is probably due both to an increase in the number of shifts the flow units make per unit time interval and to an increase in the number of flow units shifting. The limiting condition will be reached when the maximum number of flow units are all under sufficient stress to move rapidly (or frequently) with respect to each other. The total stress on the fiber at this condition will then be the maximum which one might expect the fiber to bear without rupture.

It would, therefore, seem legitimate to compare the tensile strengths for the dry cotton and dry rayon cords used (which are 3.5×10^9 and 4.5×10^9 dynes/cm², respectively) with the f_0^* values of 7.9×10^9 and 6.1×10^9 dynes/cm² calculated above. In making this comparison it must be recognized that there are undoubtedly imperfections or weak spots in the macro structure of the fibers; that the observed tensile strength is measured at a finite rate of loading at which the measured value is probably lower than the maximum strength which could be obtained in a rapid test; and that in the case of a

staple cotton cord, for which the disagreement is greatest, the tested cord strength is only about half of the potential strength of the fibers. In view of these facts, the agreement between the calculated maximum strength, f_0^* , and the observed breaking strengths suggests rather strongly that fiber breakage occurs by a mechanism involving slipping of the cellulose chains in the fiber rather than by rupture of those chains.

Effect of Temperature

The data of Table I show that as the temperature of the dry cord is increased the rate of relaxation with a given initial stress also increases. This seems to be simply the effect of high temperature increasing the frequency of shifts of the flow units, since the number of chains per flow unit remains about the same. ΔF^\ddagger increases with temperature as would be expected.

Effect of Moisture

The effect of moisture content on stress relaxation was investigated on cords which had adsorbed moisture to equilibrium at 37, 70, and 100 percent relative humidities at 25°C. Small changes in N_c/N and ΔF^\ddagger were observed with increasing moisture at low moisture contents. The effects observed with moisture adsorbed at 100 percent R.H. differed radically from those found at all other conditions.

Both the cotton and rayon relaxation curves at 100 percent R.H. showed a sharp change of slope at approximately 0.5 minute after the stretched cord had been clamped at a fixed strain (see Figures 5 and 6). These curves indicate that two stress-relaxation processes are initially occurring simul-

taneously, but that one of them is very rapid and is completed within 0.5 minute. The total stress, f , at any given time is the sum of the stress, f' , due to the rapidly decaying component and the stress, f'' , due to the slower component. Since $f'/f_0' = 0$ after 0.5 minute, it is possible to define f''/f_0' at any time from the straight-line portion of the curve between $t = 0.5$ minute and $t = 300$ minutes merely by extrapolating this portion of the curve back on the basis of the hyperbolic tangent decay curves observed previously.

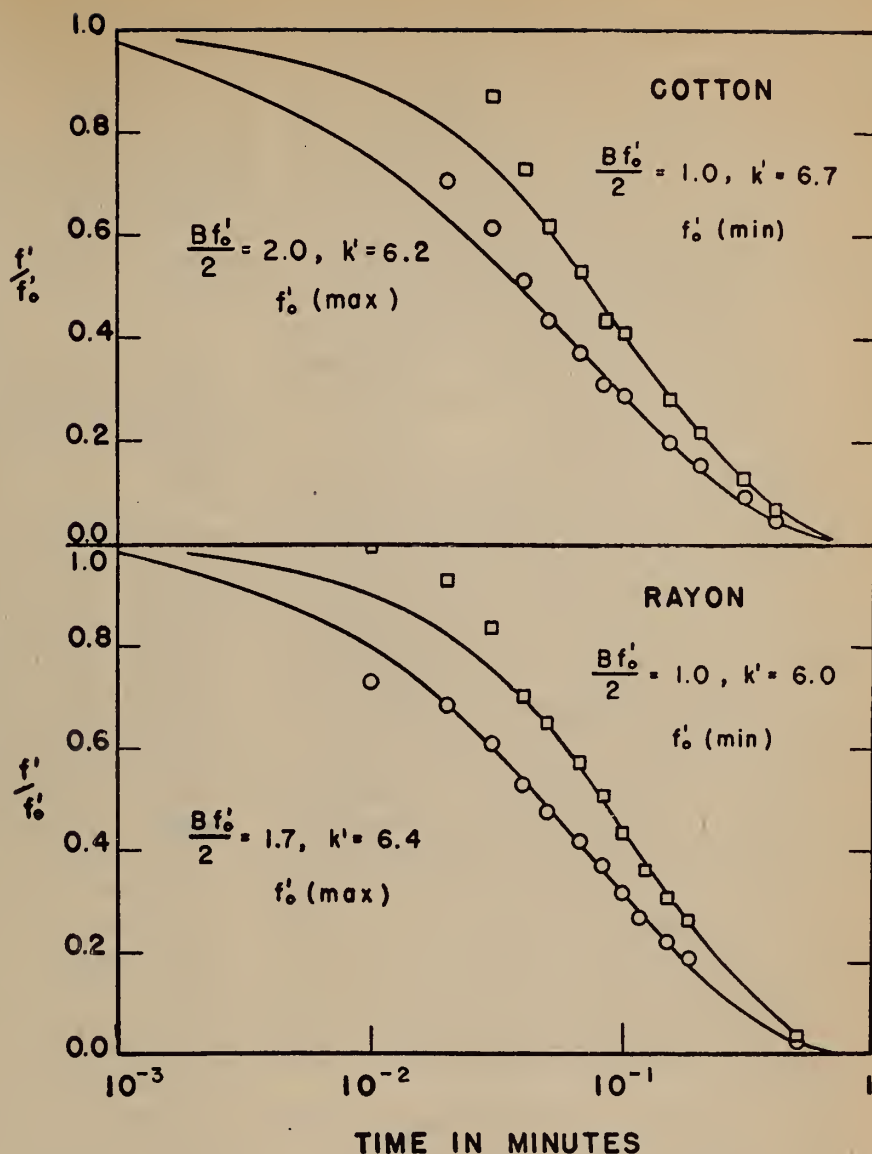


FIG. 7. Stress-relaxation curves of rapidly decaying component in cotton and rayon at 25°C and 100% R.H. Fit of theoretical curves to experimental data.

Subtraction of f''/f_0 from the observed values of f/f_0 gives a set of values of f'/f_0 from which the stress-decay curves of the rapid component may be calculated, providing we can assign a value to the initial stress fraction f_0'/f_0 of this component. Rigorous evaluation of this quantity is not possible in the present case, but its maximum and minimum values can be assigned. Then dividing f'/f_0 by either the maximum or minimum value gives $f'/f_0'_{(\max)}$ or $f'/f_0'_{(\min)}$ for various values of t , yielding data for stress-decay curves of the rapidly decaying component. These curves may be fitted to the theoretical curves for determination of the molecular constants as previously described.

Figure 7 illustrates the fit of the theoretical curves to the experimentally derived stress-relaxation data for the rapidly decaying component in cotton and rayon cords at 100 percent R.H. The fit was made for values of t greater than 0.05 minute because the observed f/f_0 at smaller values of t tended to be unreliable because of the lag in the galvanometer response to the stress signal. The calculated constants are included in Table I.

For $f_0'_{(\max)}$, the number of cellulose chains per flow unit, N_c/N , is 1.2 for cotton and 1.1 for the rayon cord; for $f_0'_{(\min)}$ the values are both considerably less than unity and, therefore, have no physical significance other than to indicate that the true value of f_0' must be approximately that of $f_0'_{(\max)}$. The slowly decaying component contains more than 10 cellulose chains per flow unit on the average. The ΔF^\ddagger values for the rapid component are of the order of 21,000 calories, about half that of the slower component.

These observations on stress relaxation at high moisture contents may be explained as follows:

Much of the water taken up by the fiber is adsorbed by the hydroxyl groups of cellulose in the noncrystalline regions, where it greatly reduces the interchain bond energies and almost completely removes any stress distribution which may exist in these areas. When stress is applied to the system, a large part of the initial stress in the noncrystalline parts is first borne by the individual chains with the shortest lengths between consecutive crystallites, forcing these chains to flow through the crystallites in the direction of stress. After some flow has taken place the chain lengths between crystalline regions become more nearly equal and the stress is distributed more uniformly among the chains so that they

move in multiples rather than as individuals. The resulting final stress inequality in the noncrystalline regions is thus less than that in the drier cords, in which the slippage of individual chains has been inhibited by the secondary hydrogen bonds between chains in the noncrystalline areas. Consequently, N_c/N for the final stress relaxation of the very wet cord is larger than that observed for the cord under any other condition.

Summary

1. The Tobolsky-Eyring reaction-rate theory of elasto-viscous behavior has been applied to stress relaxation at constant length for cotton and rayon cords.

2. The experimental data used in this application have been obtained by means of an apparatus employing the bonded metaelectric strain gage for stress measurement without necessitating change in length of the cord. Results on stress relaxation at different conditions of humidity and temperature are reported.

3. These data have been utilized in evaluating the molecular constants in the Tobolsky-Eyring theory by assuming that the flow unit in the cellulose fiber consists of multiples of the cellobiose unit.

4. The resulting constants have permitted calculation of a theoretical tensile strength which more nearly agrees with fact than that based on primary bond strength. This suggests that the mechanism of fiber breakage is one involving slippage of the cellulose chains with respect to each other rather than the rupture of primary valence bonds.

5. For the particular case of stress relaxation at 100 percent R.H. the process has been resolved into two components, the more rapid of which appears to be the limiting case in which cellulose chains are flowing as individuals.

Acknowledgment

It is a pleasure to acknowledge the suggestions and assistance of Miss Edith Honold in many phases of the experimental part of this investigation.

Literature Cited

1. Assaf, A. G., Haas, R. H., and Purves, C. B., *J. Am. Chem. Soc.* **66**, 66 (1944).
2. Blair, G. W., and Veinoglou, B. C., *Nature* **153**, 165 (1944).
3. Campbell, W. R., "Performance Tests of Wire Strain Gages: I. Calibration Factors in Tension,"

- National Advisory Committee for Aeronautics, Technical Note No. 954 (Nov., 1944).
4. Cassebaum, H., *Ann. Physik* **34**, 106 (1911).
 5. Conrad, C. C., and Scroggie, A. G., *Ind. Eng. Chem.* **37**, 592 (1945).
 6. Eyring, H., and coworkers, a series of papers on "Mechanical Properties of Textiles," *TEXTILE RESEARCH JOURNAL* **15**, 295, 451 (1945); **16**, 13, 53, 124, 201, 329, 335, 378, 382 (1946).
 7. Hermans, P. H., "Contributions to the Physics of Cellulose Fibers," New York, Elsevier Publishing Co., 1946.
 8. Hindman, H., and Krook, C. M., *TEXTILE RESEARCH JOURNAL* **15**, 233 (1945).
 9. Kohlrausch, F., *Ann. Physik* (4) **29**, 337 (1863).
 10. Leaderman, H., "Elastic and Creep Properties of Filamentous Materials and Other High Polymers," Washington, D. C., Textile Foundation, 1943.
 11. Lyons, W. J., *J. Applied Phys.* **17**, 472 (1946).
 12. Lyons, W. J., *J. Chem. Phys.* **9**, 377 (1941).
 13. Magne, F. C., Portas, H. J., and Wakeham, H., "A Calorimetric Investigation of Moisture in Textile Fibers," presented before the Division of Cellulose Chemistry at the 110th meeting of the American Chemical Society at Chicago, September 9-13, 1946.
 14. Meyer, K. H., "Natural and Synthetic High Polymers," New York, Interscience Publishers, 1942, p. 329.
 15. Meyer, K. H., and Ferri, C., *Helv. Chim. Acta* **18**, 570 (1935).
 16. Meyer, K. H., and Mark, H., *Z. physik. Chem.* **B2**, 115 (1929).
 17. Misch, L., and Picken, L., *Z. physik. Chem.* **B36**, 398 (1937).
 18. Ott, E., "Cellulose and Cellulose Derivatives," New York, Interscience Publishers, 1943, Chapter III.
 19. Ott, E., *ibid.*, p. 1045.
 20. Philipp, H. J., Nelson, M. L., and Ziifle, H. M., "The Crystallinity of Cellulose Fibers," presented before the Division of Cellulose Chemistry at the 109th meeting of the American Chemical Society at Atlantic City, April 8-12, 1946.
 21. Phillips, P., *Proc. Phys. Soc. (London)* **19**, 491 (1905).
 22. Peirce, F. T., *Trans. Faraday Soc.* **42**, 545, 560 (1946).
 23. Press, J. J., *J. Applied Phys.* **14**, 224 (1943).
 24. Smith, H. D., and Eisenschitz, R., *J. Text. Inst.* **22**, T170 (1931).
 25. Tobolsky, A. V., and Andrews, R. D., *J. Chem. Phys.* **13**, 3 (1945).
 26. Tobolsky, A. V., and Eyring, H., *J. Chem. Phys.* **11**, 125 (1943).
 27. Treloar, L. R. G., *Trans. Faraday Soc.* **36**, 538 (1940).
 28. Trouton, F. T., and Rankine, A. O., *Phil. Mag.* (6) **8**, 538 (1904).
 29. Trumpler, W. E., Jr., *J. Applied Phys.* **12**, 248 (1941).
 30. Wakeham, H., and Honold, E., *J. Applied Phys.* **17**, 698 (1946).

